

# The Changing Face of Corrosion in Coal-Fired Boilers

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It is, perhaps, an inevitable human tendency to assume, once partial insight into a particularly vexing problem has been achieved, that all aspects of that problem have been resolved for good and all. A telling example of this tendency has been the response of materials engineers to the aggressive high temperature corrosion that can occur in coal-fired utility-type boilers burning higher sulfur coals. It has long been assumed that the fundamental causes of coal-ash corrosion were well understood: that the accelerated wastage of the tube metal was triggered by the presence of molten iron-alkali sulfates that fluxed away the protective oxide film on the tube surface, thereby allowing direct reaction between the metal and reduced sulfur species in the ash. In support of this understanding of the wastage mechanism, researchers demonstrated that the rate of attack for any given material was critically dependent on the surface metal temperature, with the most rapid attack occurring within a temperature range where the molten sulfates were stable. Either above or below this temperature range the rate of attack diminished significantly, because the molten species outside the range were not stable.

Armed with this understanding, the materials engineers quickly recognized that there were at least two potential options for effectively mitigating the effects of the coal ash attack. One option was to lower the outlet steam temperature of the boiler to a level where the surface metal temperature of the affected components would not support the formation of the molten phase. Following the experience at Eddystone Unit 1, this became the default option for the entire power industry in the US, and it is one of the primary reasons that US utilities have shown so limited an interest in the more advanced steam conditions that could significantly improve the overall efficiency of the generating cycle. An alternative method of combating the effects of coal-ash corrosion was to install a material that contained a sufficient amount of oxide stabilizing elements, such as chromium, silicon, or aluminum, to resist the dissolution of the film when the molten phase was present. For example, it was shown that at temperatures between 600°C and 650°C in an aggressive coal-ash environment, a chromium content in excess of 25% could confer superior resistance to the attack. Silicon could provide similar resistance to coal ash attack when present in amounts between 2 and 14 weight%, while an aluminum content greater than 4% generally was shown to be beneficial.

Over the past ten to fifteen years, a period coinciding with the widespread implementation of modified firing systems in boilers to control NOx emissions, there have been a number of failures in boiler tubing that have not fit the classic “coal-ash” corrosion mold. In particular, rapid rates of attack have been observed in materials normally resistant to the effects of coal-ash corrosion, and the attack has occurred at temperatures below those where the most aggressive reactions would be expected. For

example, HR3C tubing (a modified TP310 austenitic alloy with 25% chromium) installed in the reheater of a supercritical boiler with an outlet steam temperature of 1005°F suffered rapid attack immediately upon initial operation. Rates of wall loss, which were in excess of 30mpy, were unchanged from the rates of attack experienced by TP304H, a less resistant alloy containing 18% chromium. An analysis of the ash deposit in these failures has provided at least partial insight into the likely cause of the unexpected attack, and the failures, themselves, have highlighted the complex interactions that exist between fuel composition, boiler operation, and the resulting environment that ultimately govern component life.

A common feature of the ash deposited on the surface of tubes that have shown the anomalous corrosion behavior has been an unusually high level of carbon, and the presence of the carbon in the ash provides partial insight into the way in which changes in firing have dramatically altered the boiler environment. The source of the carbon is believed to be particles of fuel that are not consumed as they pass through the combustion zone, a phenomenon influenced by such factors as low levels of oxygen in the combustion zone and inadequate fineness of the coal particles coming from the mills. When these unburned particles become embedded in the ash deposited on the surface of a reheater or superheater tube (or furnace wall tubes), then the nature of the deposit is radically altered. It is suspected that the carbon reacts with CO<sub>2</sub> to generate high levels of CO that then are concentrated at the interface between the deposit and the tube surface. The result is the production of a highly localized and highly reducing “micro-climate” in an area of the boiler where the bulk flue gas composition should be oxidizing in nature. This local “micro-climate” can achieve a sufficiently high carbon potential, through adsorption and decomposition of the CO molecule at the metal surface, that carbon then is able to diffuse into the metal lattice. Once diffused into the lattice of a higher chromium alloy, the carbon preferentially combines with the chromium to form chromium carbides, a phenomenon that has been observed with increasing frequency at the outer surface of superheater and reheater tubes that have suffered accelerated attack. The formation of the carbides reduces the chromium available to the matrix to stabilize the protective oxide film. The result is a breakdown of the protective film and rapid sulfidation in an alloy that under classic coal-ash conditions would be immune to attack.

It is by no means the case that all features of this altered environmental condition are fully understood and the appropriate corrective strategies identified. Response to this problem has largely been to treat the symptoms: that is, apply more highly alloyed materials, such as the 45Cr-55Ni alloy, either as weld overlay or as thermal spray, to the surface of the tubing in the areas affected. However, the economic consequences of this approach can be significant. For example, a recent installation in which the 45Cr-55Ni weld overlay was applied to replacement reheater tubes to combat this “new” form of coal-ash corrosion resulted in a tenfold increase in the cost of the replacement compared to use of the original stainless steel material. It is imperative, therefore, that a better understanding be gained of the ways in which changes in firing conditions in coal-fired boilers – changes dictated by increasingly stringent restrictions on emissions – have altered the internal environment of the combustion chamber and the subsequent flue gas passages. Proposals have been made to the Department of Energy/Ohio Coal Development Office consortium currently investigating the materials-related implications of operating an ultra-supercritical boiler at outlet steam conditions of 1400°F to

investigate this and similar “new” phenomena in greater depth. It is to be hoped, therefore, that in the coming years the complex links between boiler operation, fuel chemistry, and corrosion will be more fully understood and economic solutions to the corrosion issue identified. Only if such an understanding is gained will it be possible to operate the next generation of coal-fired boilers at the advanced steam conditions that an increasingly regulated market will demand.